

Dendrite-Growth Morphology Modeling in Liquid and Solid Electrolytes

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Project ID: bat328

Overview

Timeline

- Project start date: 01/01/2017
- Project end date: 12/31/2019
- Percent completed: 70%

Budget

- Total project funding:
\$1,135,125
 - DOE share: \$999,943
 - Contractor share: \$135,182
- Funding for FY2018: \$337,023
- Funding for FY2019: \$310,816

Barriers

- Li metal film electrodes with
- Dendrite growth
 - Low coulombic efficiency
 - Short calendar and cycle life

Partners

- Interactions/collaborations
 - Gary Rubloff (UMD) :
Coating development
 - Katherine Jungjohann : SNL-ALBQ
In situ TEM, liquid cell
- Project lead, Yue Qi (MSU)

Relevance / Objectives

Overall Objective

- Develop a validated multi-scale model to predict Li dendrite morphology evolution in both liquid and solid electrolytes LIBs during electrodeposition and stripping, in order to *accelerate the adoption of Li metal electrodes in current and emerging battery technologies.*

Technical Target

- An atomically-informed, fully-coupled electrochemical-mechanical dendrite morphology evolution model that allows us to design the desired properties of artificial SEI coatings, the microstructure of solid electrolyte materials, and the corresponding battery operating conditions, so as to avoid dendrite growth during cycling.

Impacts

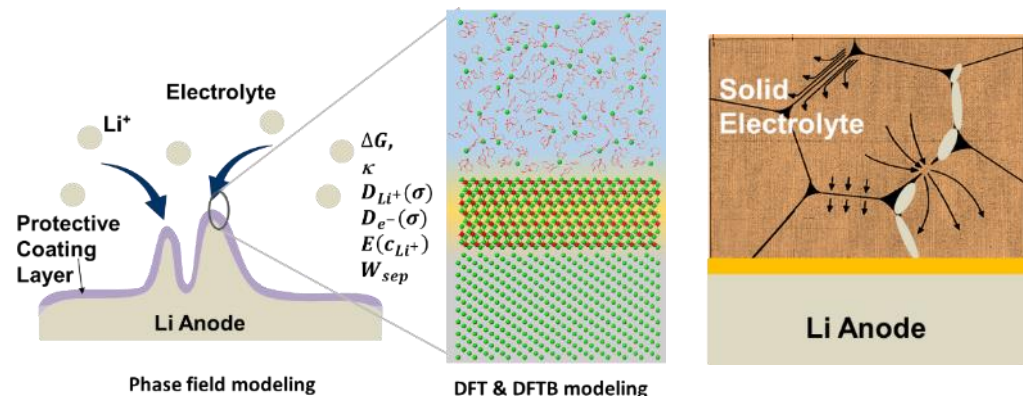
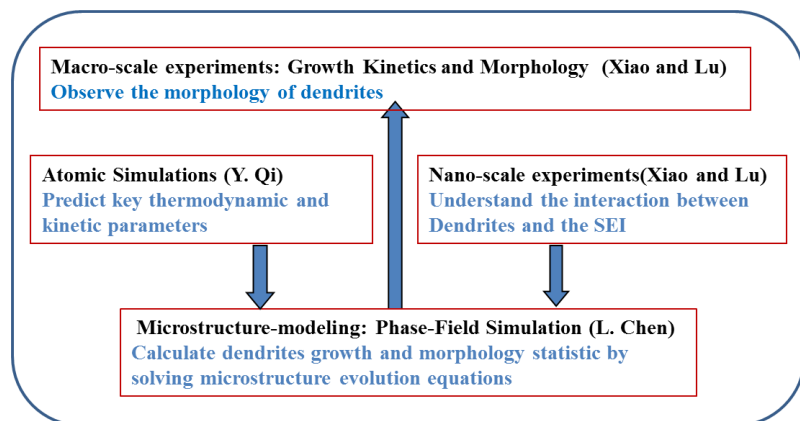
- Enable the design of durable and safe Li-anodes for high energy density lithium rechargeable batteries that can meet DOE's target for EV applications $>350 \text{ Wh/kg}$ & $<\$100/\text{kWh}_{\text{use}}$.

2019 Milestones

Month /Year	Milestone of Go/No-Go Decision	Status
Dec. 2018	<p>Identify an ideal microstructure of LLZO to avoid Li dendrite growth.</p> <p>*It was predicted a coating layer, such as LiPON, between the Li/LLZO, will be more efficient in resisting Li dendrite. A Go decision was made to experimentally verify this prediction.</p>	Go
Mar. 2019	A fully coupled Li/SEI/liquid electrolyte dendrite morphology model is developed.	completed
Jun. 2019	The relationship between Li/SEI interface roughness, adhesion, and dendrite morphology in a liquid electrolyte is illustrated.	In progress
Sep. 2019	Determine the effect of multicomponent SEI layer on dendrite morphology in a liquid electrolyte.	In progress

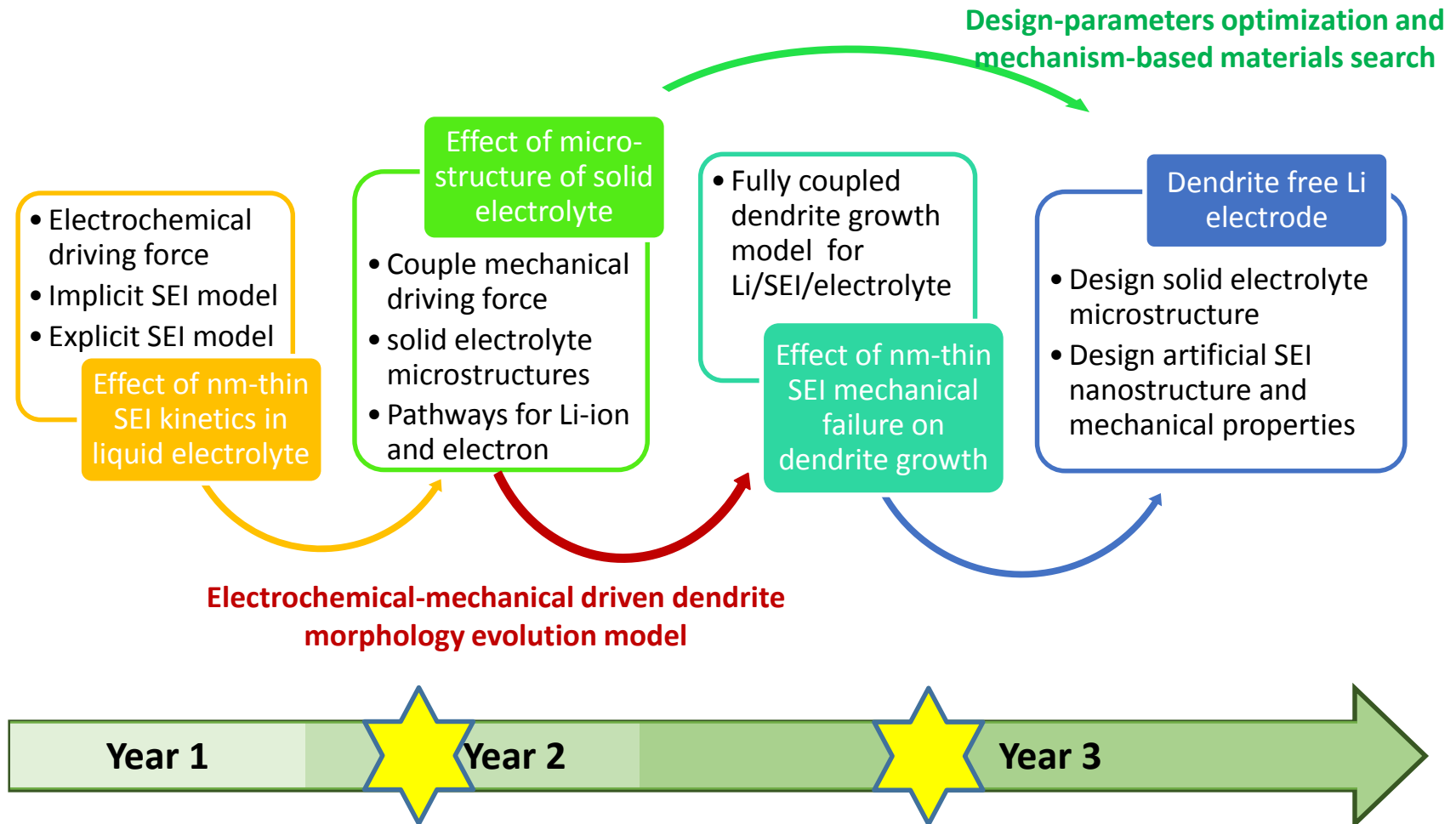
Multiscale Modeling and Experimental Approach

- **Formulate** a general framework that captures the electrochemical-mechanical driving forces for Li morphology evolution.
- **Consider** the role of the *nm-thin SEI* in liquid-electrolytes as well as the microstructures of *$\mu\text{m-thick}$* solid-electrolytes for Li morphology evolution.
- **Connect** micron-scale **phase-field models** and **atomic-scale DFT-based** simulations via parameter- and relationship-passing in order to predict *Li dendrite nucleation and growth kinetics and morphology*.
- **Validate** the key input parameters and main conclusions of the multi-scale model as new capabilities being developed step-by-step.



Model Development Strategy and Timeline

Model liquid and solid electrolytes in order to couple electrochemical-mechanical driven dendrite growth step-by-step

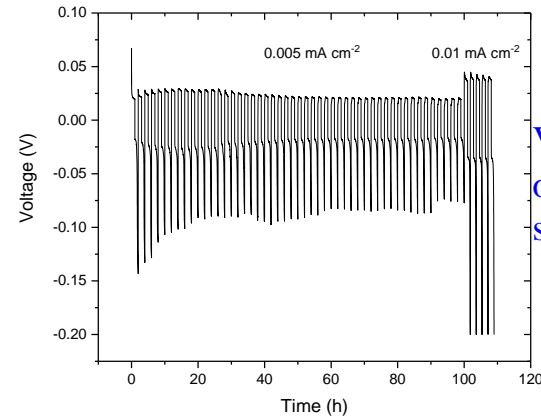
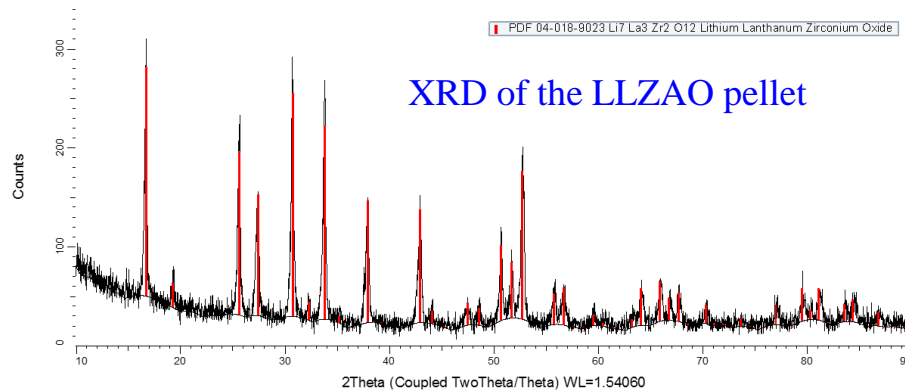


Outline and the Accomplishments

- Developed a new **explicit** model to simulate Li dendrite formation and growth inside **solid electrolytes** with microstructure and internal defects
 - Experimentally observed Li dendrites intergranular propagation inside the LLZAO
 - Discovered the surfaces (pore and cracks) band gap is lower than that in the bulk in some solid electrolytes and the surfaces can trap excess electrons in LLZO, via DFT calculations
 - Incorporated the new electron trapping mechanism in the phase field model by introducing surface electron density and explicit dendrite nucleation process.
 - Determined the key material properties that impact Li dendrite growth inside of the solid electrolytes
 - Revealed the electrons trapped on the internal defect surfaces accelerate Li dendrite growth and allow isolated Li nucleation to occur, leading to non-uniform dendrite growth
- Successfully transferred the learning from solid electrolytes to SEI design **in liquid electrolyte**
 - Electron trapping mechanism – similar to that in LLZO – was found on the cracked surface of Li_2O but not Li_2S
 - Experimentally stabilized the SEI of Li metal electrode with sulfite-based additives by forming Li_2S , which is also mechanically more stable due to its volume compatibility with Li.

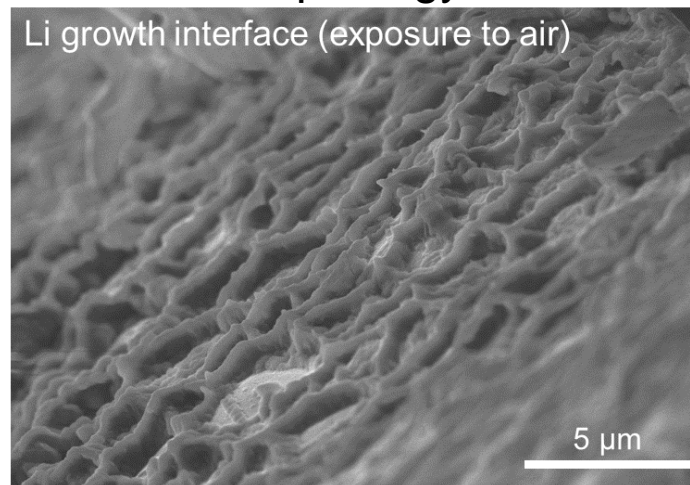
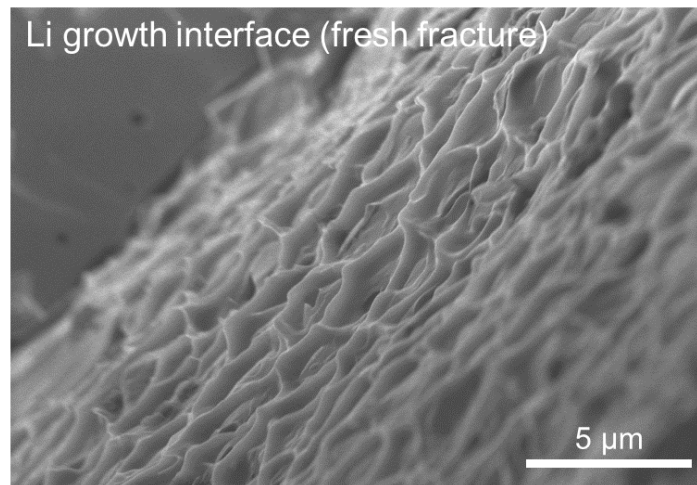
Accomplishment 1.1 Observed Li dendrites intergranular propagation inside the LLZAO sample

- Prepared $\text{Li}_{6.25}\text{La}_3\text{Zr}_2\text{Al}_{0.25}\text{O}_{12}$ (LLZAO) pellets and tested in Li|LLZAO|Li cell



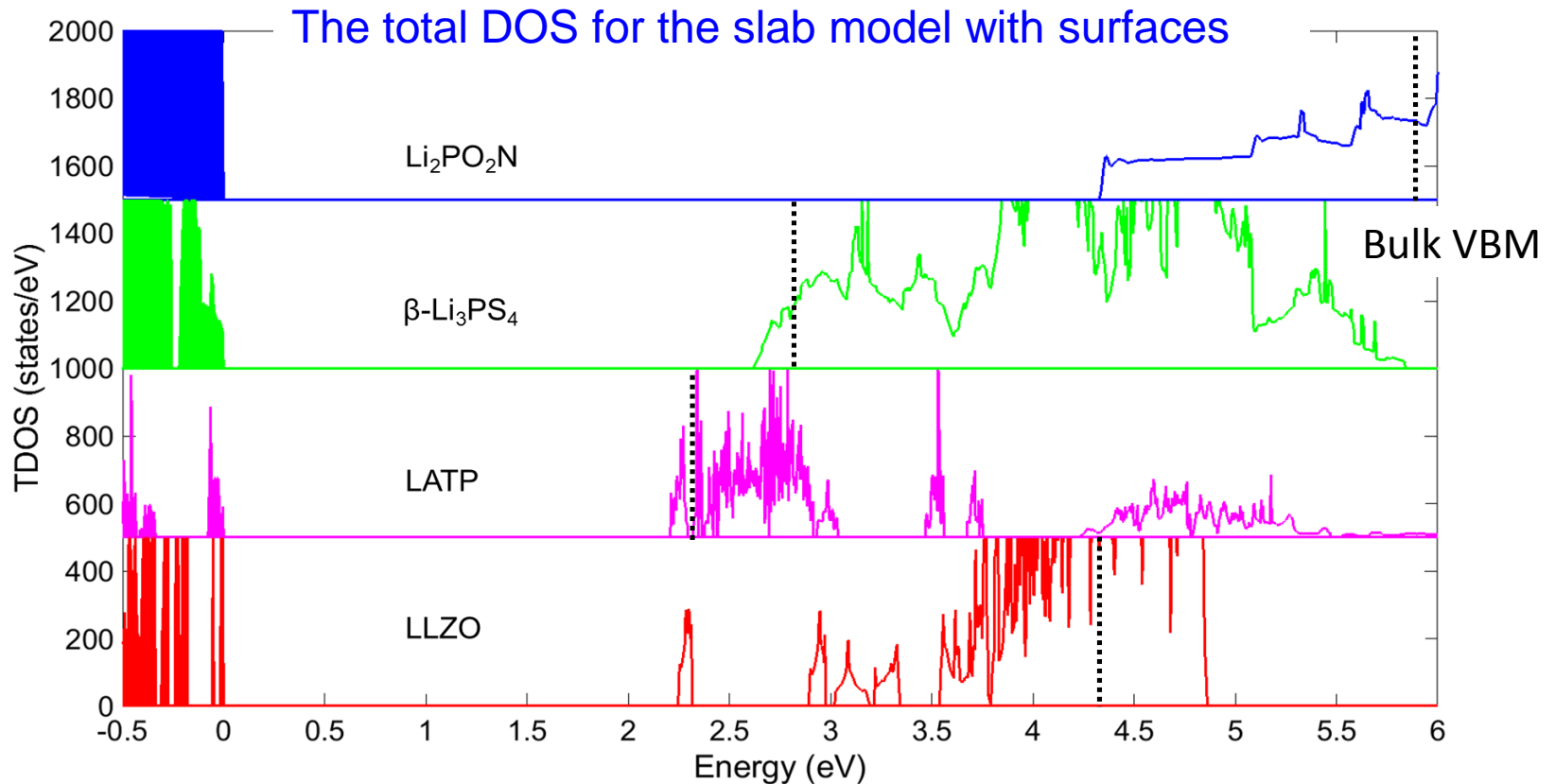
Voltage profiles of a Li|LLZAO|Li symmetrical cell

- Observed several black lines (dendrites) in the pellet after short circuit, which occurs above the critical current density (CCD) of $\sim 0.025 \text{ mA cm}^{-2}$.
- Fractured the LLZAO sample at the Li dendrite location and took SEM images of the cross section to observe the Li dendrite morphology.



Accomplishment 2.1: Discovered the surface (pore and cracks) band gap is lower than that in the bulk in some solid electrolytes

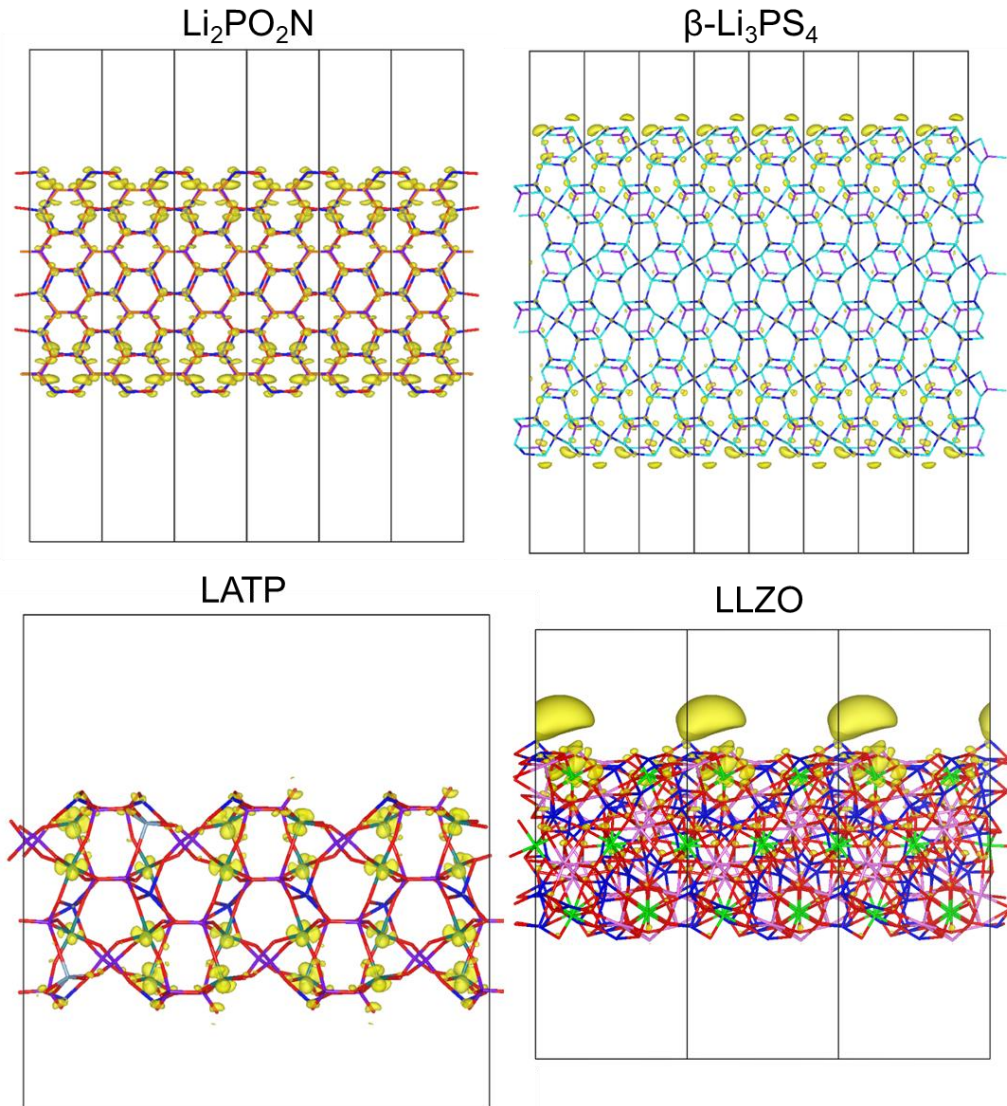
- Used slab model with surfaces to represent **internal defects** (pores or cracks)
- Determined the **surface** structures and analyzed the density of states (DOS) with DFT calculations for several important solid electrolyte materials



**The dashed line represents the valence band maximum of a perfect crystal (bulk)*

Accomplishment 2.2: Discovered the surfaces (pore and cracks) can trap excess electrons in LLZO

- The location of excess electrons (same areal density) in the slab model



- The band gap dropped dramatically in LLZO, and dropped slightly in Li₃PS₄ and LATP, making these surfaces more electronically conductive than their bulk.
- Li₂PO₂N still maintained a large bandgap on the surface.
- Large amount of excess electrons were trapped on LLZO surface, consistent with the additional surface electronic state.

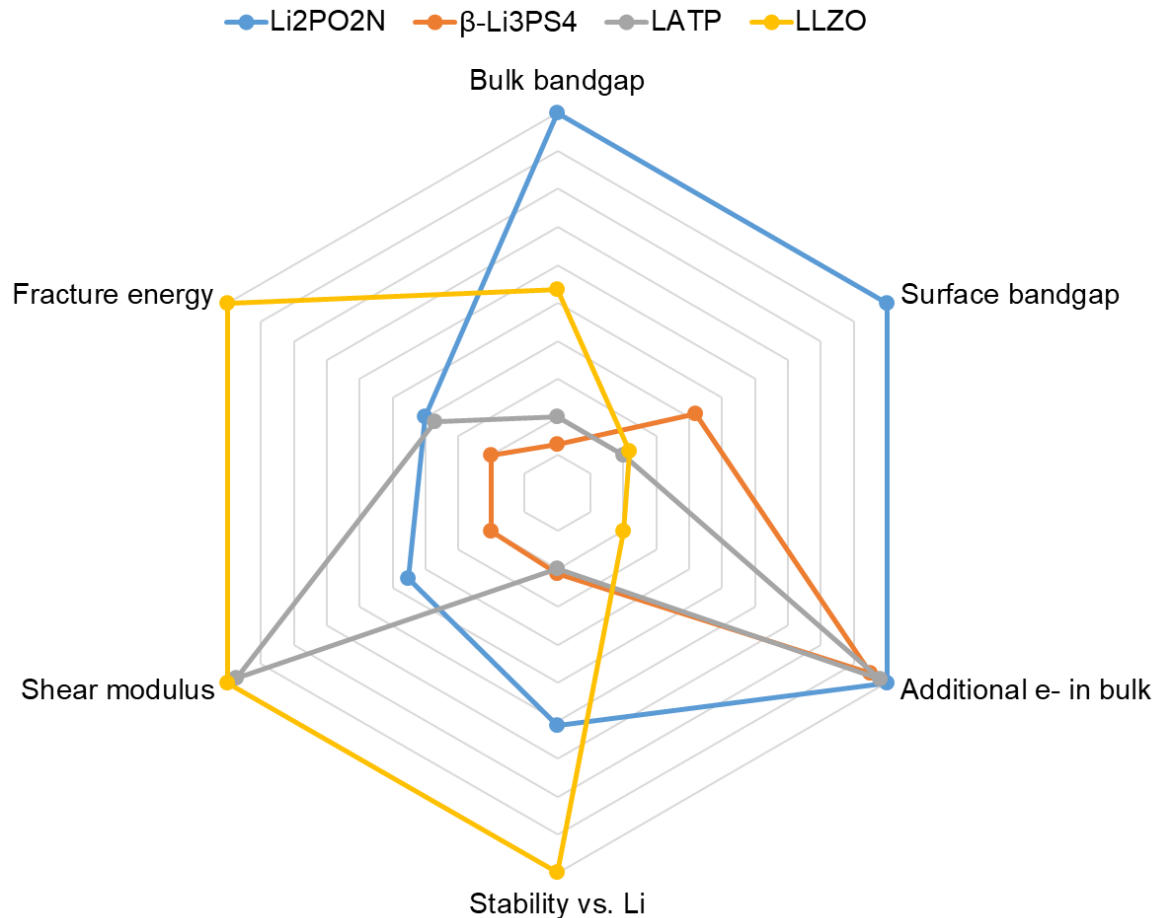
Accomplishment 2.3: Determined the key material properties to impact Li dendrite growth inside of the solid electrolytes

	Shear Modulus (GPa)	Fracture Energy (J/m ²)	Reduction Potential vs. Li (V)	Bulk Bandgap (eV)	Surface Bandgap (eV)	Location of excess electrons
Li ₂ PO ₂ N <small>[Herbert, E.G. et al., <i>Thin Solid Films</i>, 520(1), pp.413-418]</small>	30	0.92	0.87	5.98	4.35	Bulk - O
β -Li ₃ PS ₄ <small>[Baranowski, L.L. et al., <i>ACS applied materials & interfaces</i>, 8(43), pp.29573-29579.]</small>	6	0.38	1.71	2.82	2.67	Bulk - S,P
LATP <small>[Deng, Z. et al., <i>Journal of The Electrochemical Society</i>, 163(2), pp.A67-A74.]</small>	57.6	0.88	2.16	2.36	2.20	Bulk - Ti
LLZO <small>[Ni, J.E. et al., <i>Journal of Materials Science</i>, 47(23), pp.7978-7985.]</small>	59	1.72	0.05	4.30	2.24	Surface - La

- By reviewing **15** experimentally reported CCD, the resistance of solid electrolytes to Li dendrite growth inside was ranked as
 - LiPON (Li₂PO₂N) \approx LATP > β -Li₃PS₄ > c-LLZO.
 - The higher CCD in LATP is due to the insulating interphase layers formation.
- As reported by F. Han et al., *Nature energy*, 2019., the dendrite resistance follows the opposite trend of electron conductivity as: LiPON (Li₂PO₂N) > β -Li₃PS₄ > c-LLZO.
- The DFT predicted resistance to Li dendrite: **Li₂PO₂N > β -Li₃PS₄ > LATP > LLZO**

Accomplishment 2.3: Determined the key material properties to impact Li dendrite growth inside of the solid electrolytes

Compare to other material properties, the internal defect band gap and the distribution of the excess electrons dominate the Li dendrite growth



Normalization method for each property

$$X' = \frac{X - X_{\min}}{X_{\max} - X_{\min}}$$

Predicted Li dendrite resistance: LiPON (Li₂PO₂N) > β-Li₃PS₄ > LATP > c-LLZO

Achievement 3.1 Developed the multiscale approach to model Li dendrite growth in solid electrolytes

Previously Established in the phase field model

- Implemented nonlinear phase field model for $Li^+ + e^- \rightarrow Li(s)$
- Coupled elasticity and electrochemistry
- Described the microstructure of the solid electrolyte

New Development:

- Incorporated the new electron trapping mechanism by introducing surface electron density and explicit dendrite nucleation process.
- Formulated the new Li metal phase evolution equation

$$\frac{\partial \xi}{\partial t} = -L_{\sigma}^{\xi} \left[\frac{\partial f_{ch}}{\partial \xi} - \kappa_{\xi} \nabla^2 \xi + \frac{\partial f_{mech}}{\partial \xi} \right] - L_{\eta}^{\xi} h'(\xi) \left[-c_{Li} + \textcolor{red}{c}_e \exp \frac{-\alpha n F \eta_a}{RT} + \exp \frac{(1 - \alpha) n F \eta_a}{RT} \right] + \omega \cdot \delta_n(\textcolor{red}{c}_e)$$

Elasticity

Electrochemical
driving force

Dendrite
nucleation

- Estimated the excess surface electron concentration in LLZO by integrating the DFT computed DOS of a slab model, $\textcolor{red}{c}_e = 0.337 \text{ mol L}^{-1}$
- Assumed internal defect surfaces (pores, grain boundaries, junctions) share the same c_e (DOS calculations for GB structures are needed)

Modeling Results: Assumed no electron trapping on the internal defect surfaces, observed uniform growth with smaller grain size

Assume:

Li dendrite growth inside a polycrystalline (similar to) LLZO

No trapped electrons on internal defect surfaces (pores, GBs, junctions)

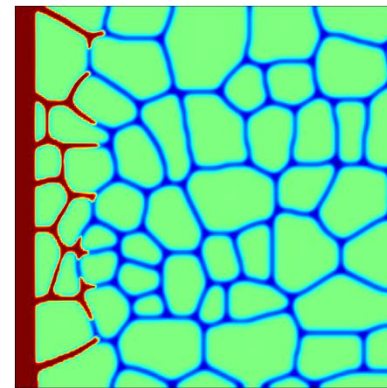
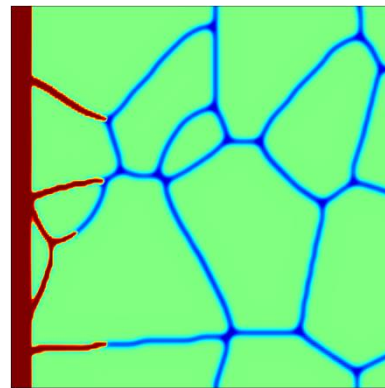
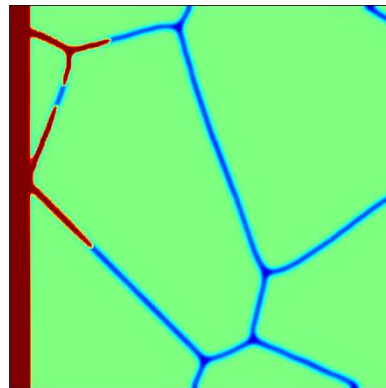
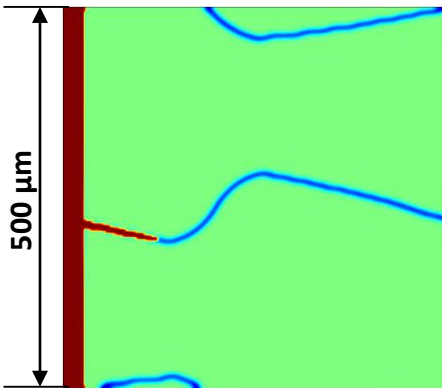
Grain size (μm)

500

300

150

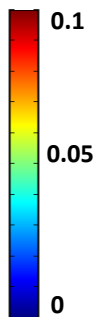
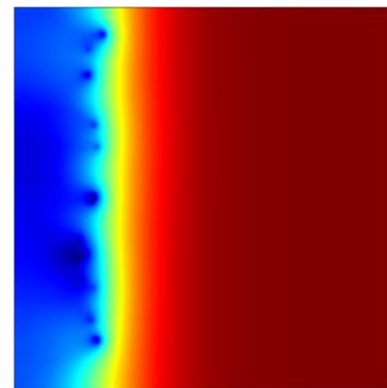
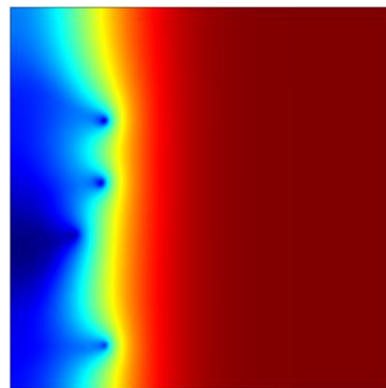
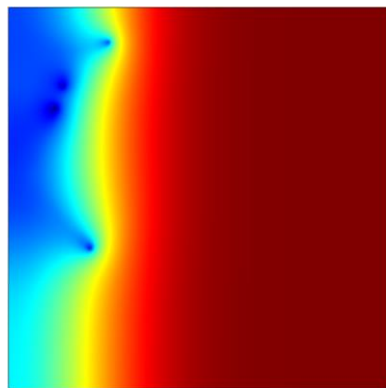
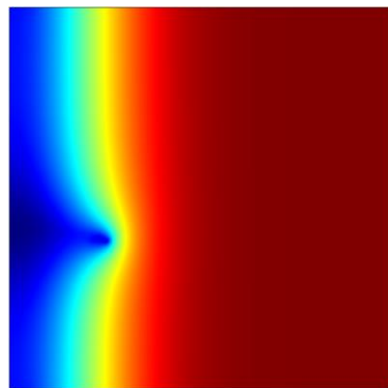
75



Colors of phases



Electric Potential (V)



Modeling Results: With trapped electrons, isolated Li nucleation occurred. Dendrite growth is non-uniform

Assume:

Li dendrite growth inside a polycrystalline (similar to) LLZO

Trapped electrons on internal defect surfaces (pores, GBs, junctions)

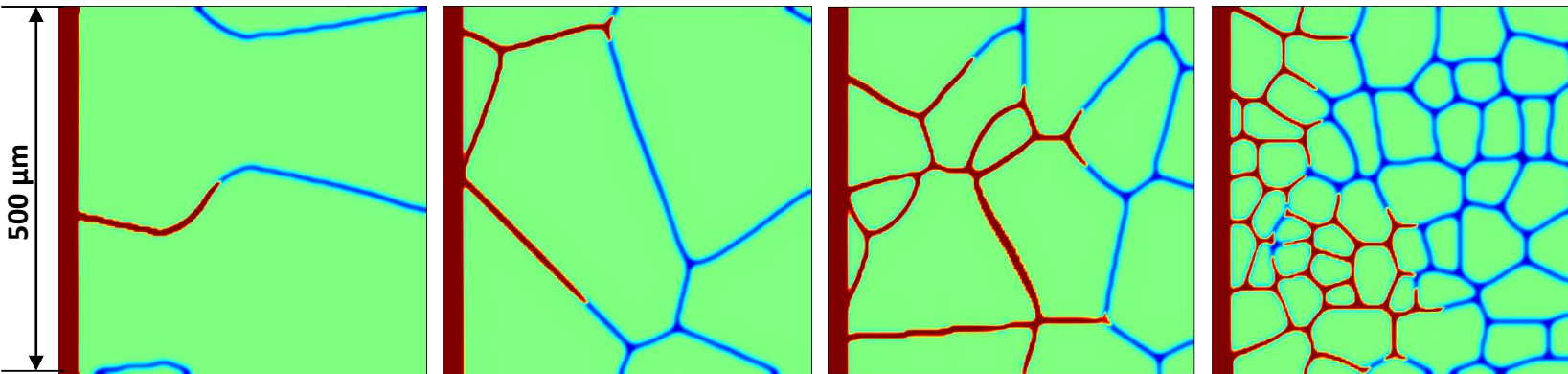
Grain size (μm)

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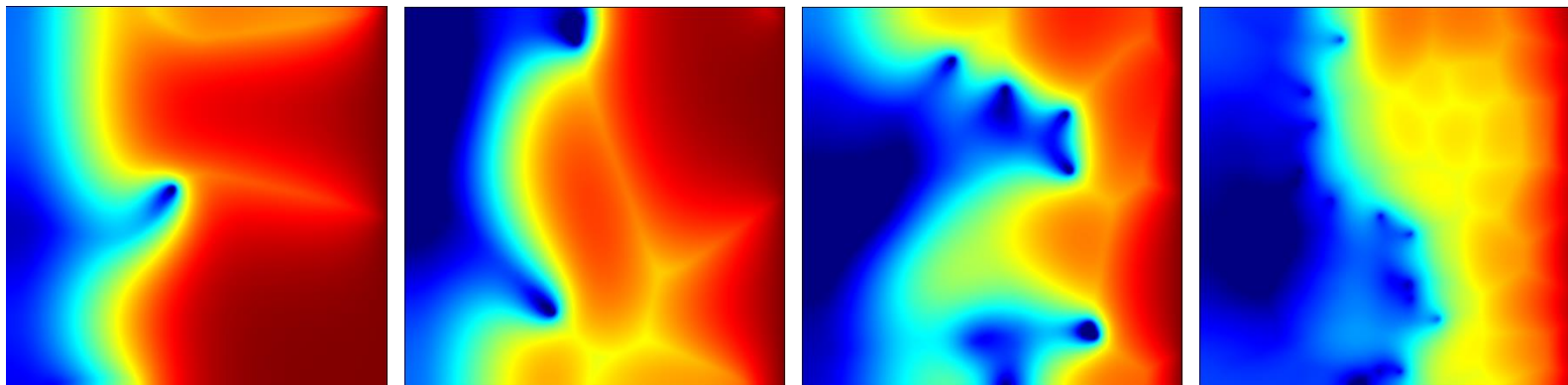
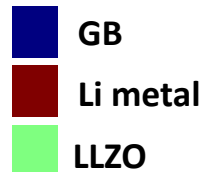
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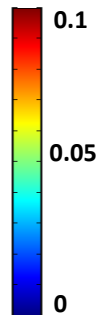
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Colors of phases

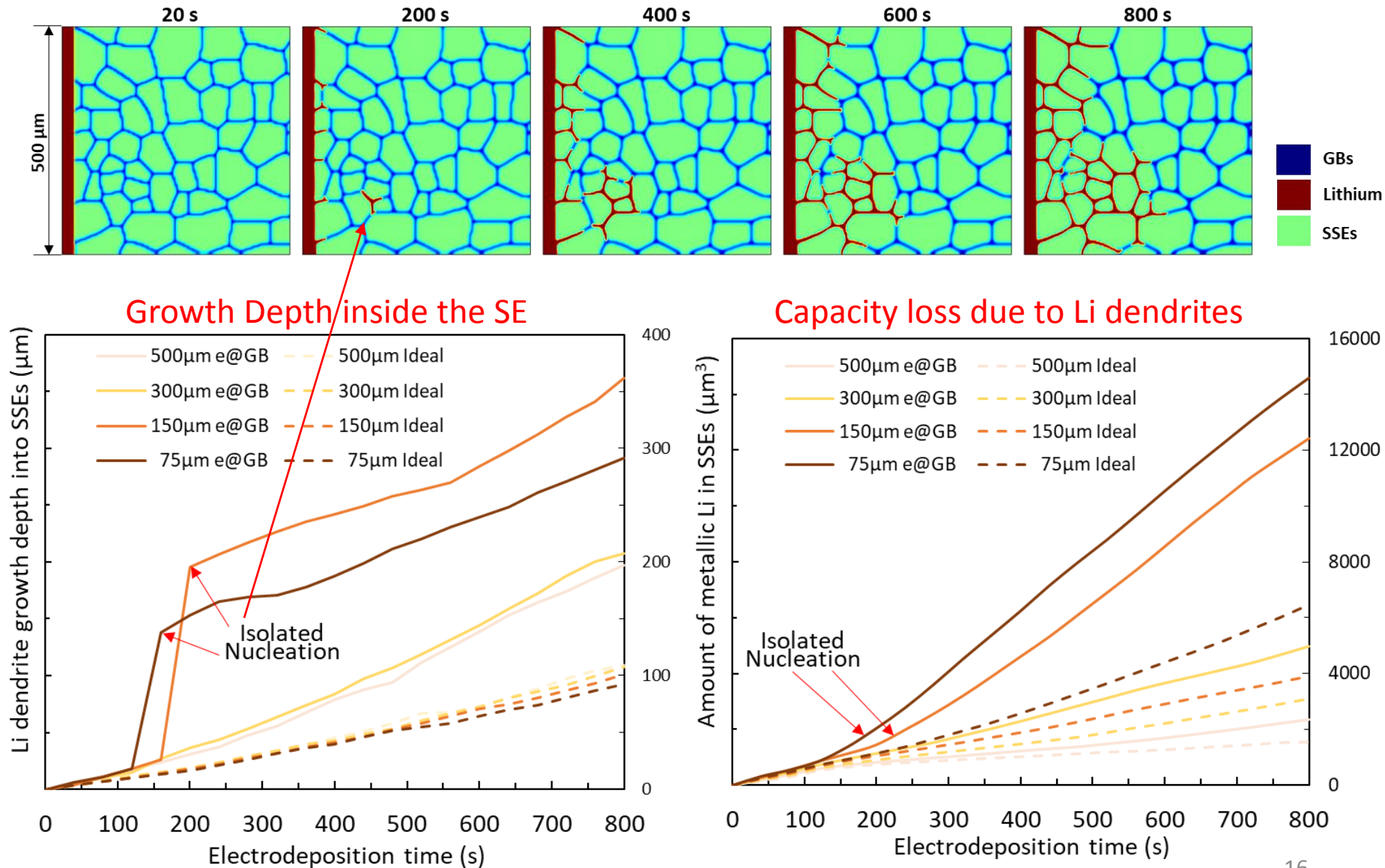


Electric Potential (V)

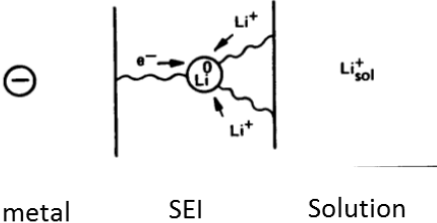
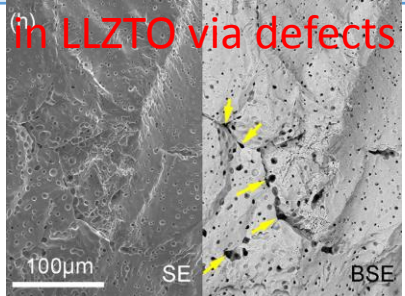


Isolated Nucleation

Achievement 3.2 Revealed the electrons trapped on the internal defects surfaces ($e@GB$) accelerate Li dendrite growth

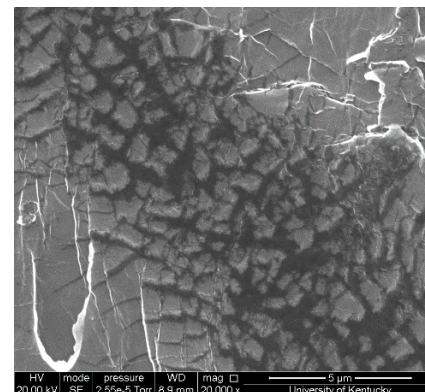
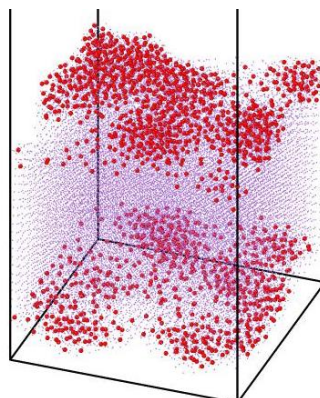
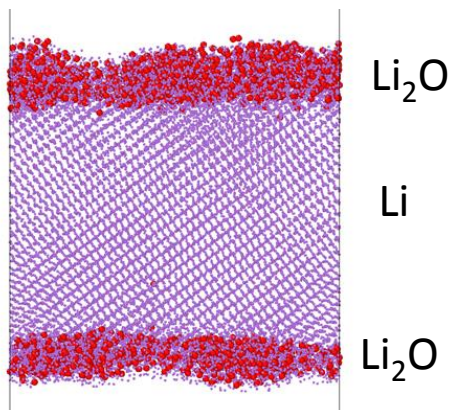


Compare liquid and solid electrolyte to understand the role of SEI in dendrite growth

	Growing in liquid electrolytes	Growing in solid electrolytes
Knowledge Transfer	<p>→ The effect of the nm-thick protective SEI layer (exist in both)</p> <p>The effect of the microstructure (easier for experiment) ←</p>	
Key phenomena	 <p><i>E. Peled, Lithium batteries, edited by Jean-Paul Gabano. 1983, London, Academic Press,</i></p>	<p>Li⁺ in LLZTO via defects</p>  <p><i>Y. Ren et. al, Electrochemistry Communications 2015, 57, 27</i></p>
Modeling approach	Implicit model (parameterize SEI properties) in the multiscale dendrite growth model	Explicit model (resolve microstructures and defects, pores, boundaries) to simulate Li dendrite formation and growth in a solid electrolytes
Common	Common functionality (electronically insulating; Li ion conducting, stable)	
Different Atomistic Details	Li ⁺ and e Transport at the Li/SEI/liquid-electrolyte interface	Li ⁺ and e transport at the SE surface and boundaries
Phase-field model similarities	Governing equations, Butler-Volmer kinetics, Charge carrier (electron and Li-ion) transport, include microstructure details, track microstructure evolution	

Some SEI component, such as Li_2O , are not good passivation layers on Li due to volume shrinkage induced crack generation

- ReaxFF simulation of Li/ Li_2O interface formed by oxidized



MD simulations show oxide **cracked during growth**

SEM by YT Cheng @ UKY

- PB-ratio (PBR) can be used as an empirical relation for mechanical stability

$$R_{\text{PB}} = \frac{V_{\text{oxide}}}{V_{\text{metal}}}$$

PBR < 1, coating easily breaks;

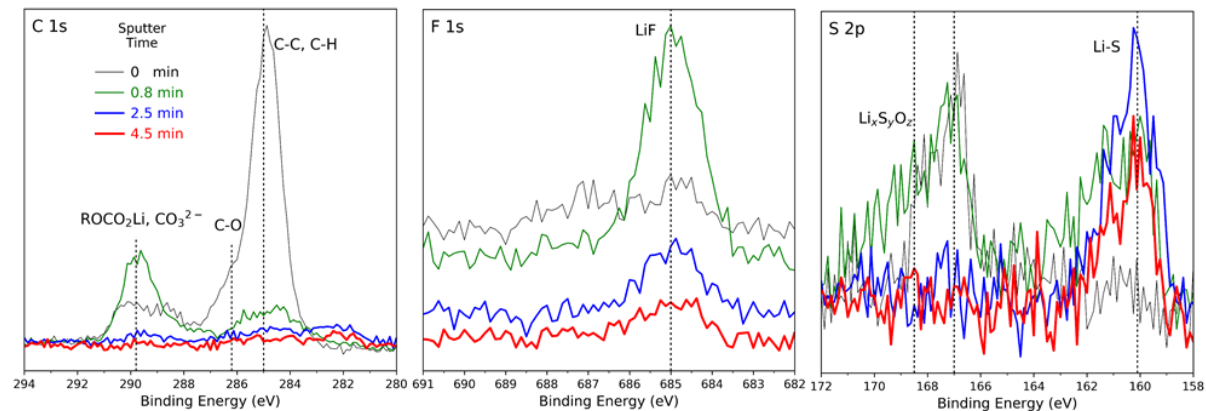
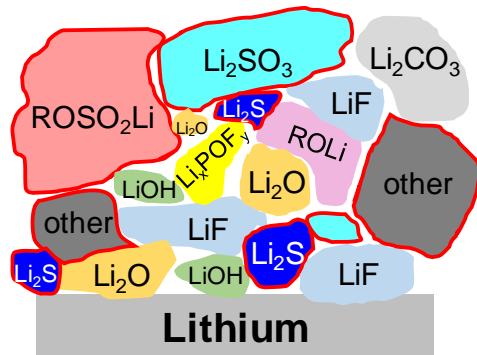
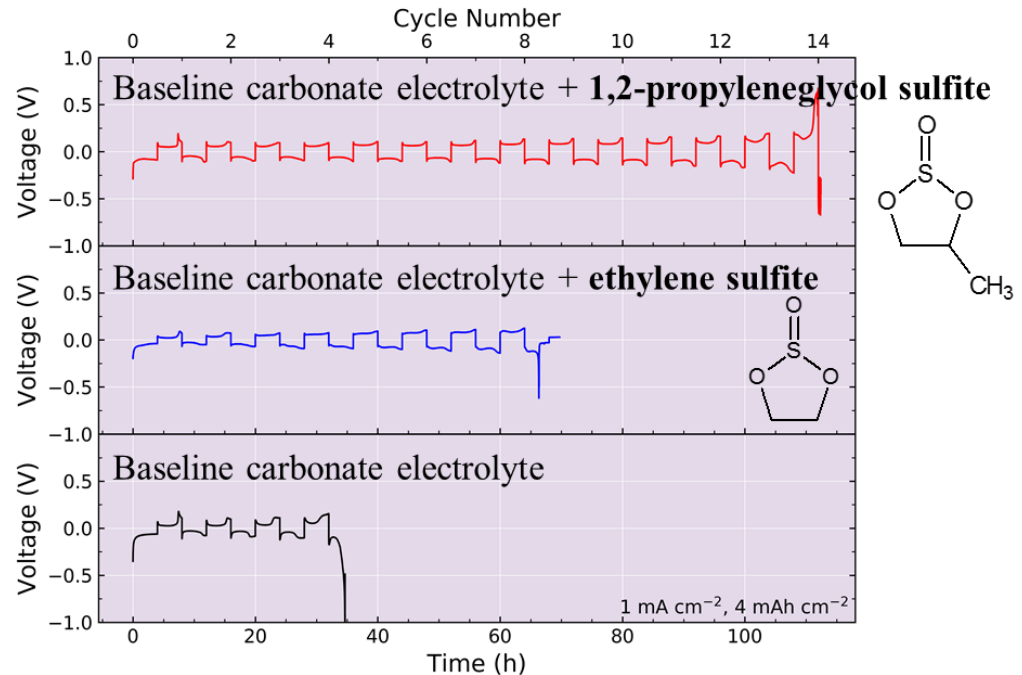
PBR > 2, coating delaminates;

1 < PBR < 2, the coating passivates
(Al_2O_3 PBR~1.3 on Al).

compound	Volume (\AA^3) /Li	PBR
Li_2O	11.9975	0.596
LiF	16.7772	0.834
Li	20.1239	1.000
Li_2S	23.4105	1.163
Li_2CO_3	25.2371	1.254

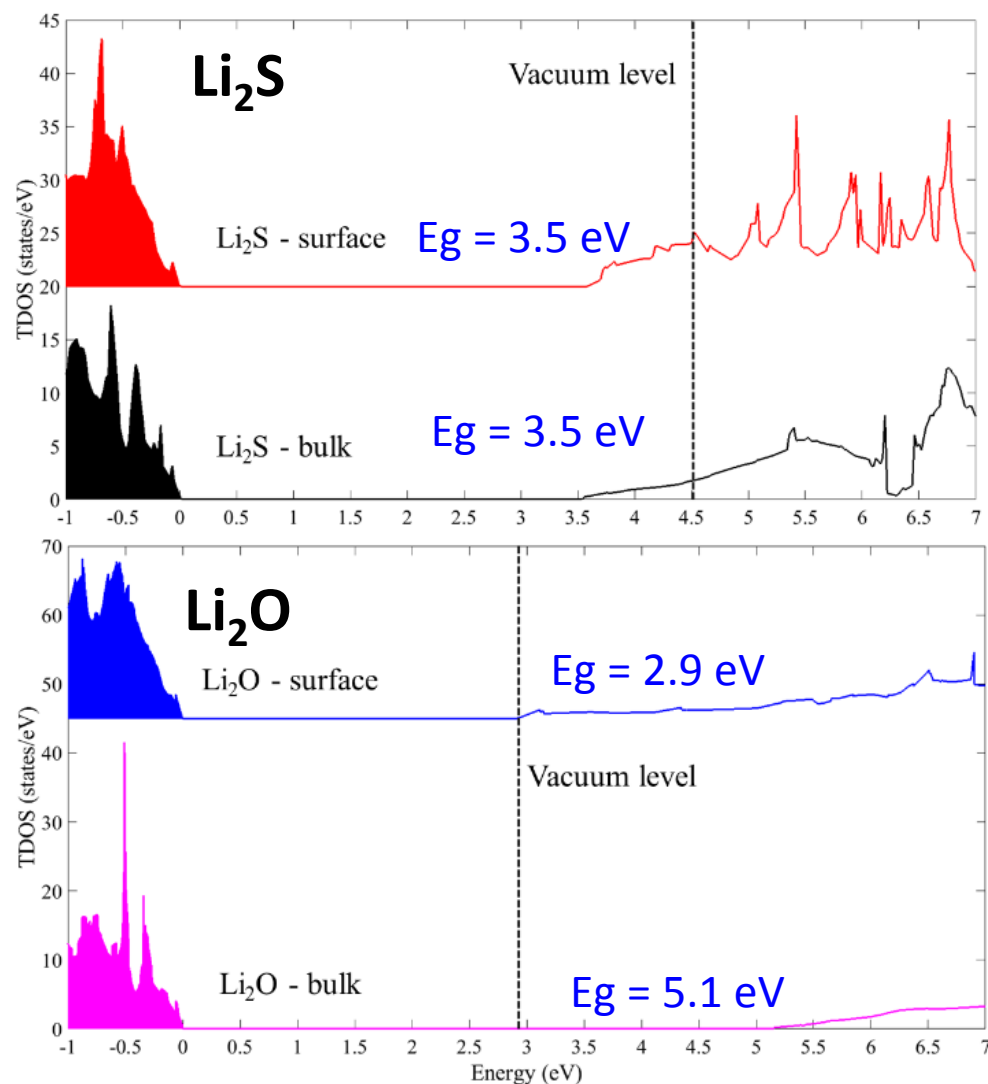
Achievement 4.1 Experimentally Stabilized the SEI of Li Metal Electrode with Sulfite-Based Additives by forming Li_2S

- 5wt% sulfite-based additives can elongate the cycle life under a harsh cycling condition (4 mAh cm^{-2}) in the conventional 1 M LiPF_6 EC/DEC electrolyte.
- Li_2S was found near the Li. Together with LiF , its existence is likely to enhance the mechanical stability of SEI film.

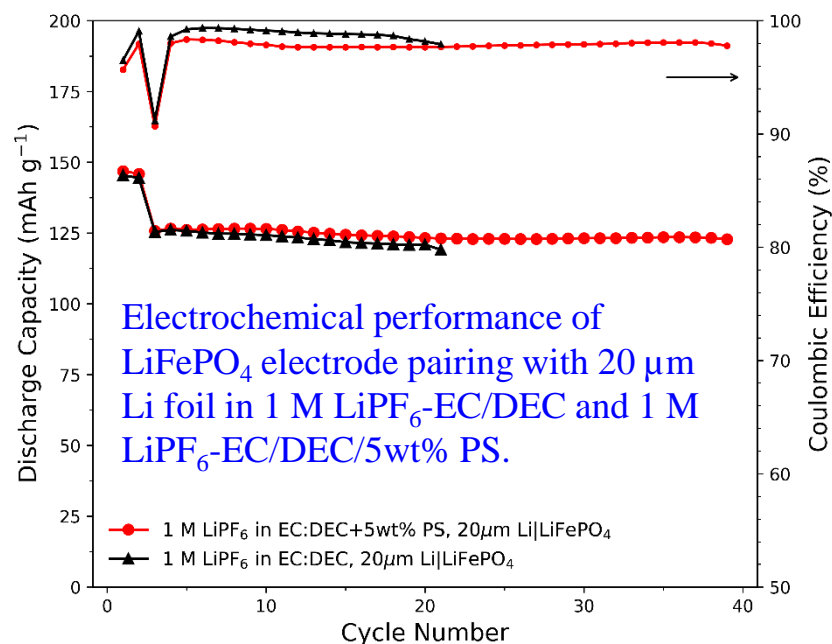


XPS depth profile spectra

Achievement 4.2 Electron trapping mechanism – similar to that in LLZO – was found on the cracked surface in Li_2O but not Li_2S



Successfully transferred the learning from solid electrolytes to SEI design



The surface band gap dropped 2.2 eV in Li_2O due to its low work function.

Responses to Previous Year Reviewers' Comments

Q: The reviewer wondered whether the model to be developed will predict the critical factors that govern the nucleation and growth of Li dendrites.

A: This has been implemented this year.

Q: In addition, correlations between the calculated results and experimental results should be discussed as well as performing more experiments to confirm the results from models.

A: We are doing so. Some predictions are being tested, for example, LiPON coated LLZO.

Q: The reviewer encouraged the team to engage with the Battery 500 Consortium R&D teams.

A: We are looking for the opportunities and mechanisms to do so.

Q: The reviewer questioned the fact that, in the team's report, only two papers are shown as published, and three manuscripts submitted. With such a strong team, the reviewer said it is desirable to see more products.

A: 8 more papers were published or accepted during this review period and 3 more were submitted.

Collaboration and Coordination with Other Institutions

Gary Rublof University of Maryland (DOE NEES EFRC)	Apply ALD LIPON coating, which has higher Li conductivity compared to typical SEI components, such as (LiF, Li ₂ O, Li ₂ CO ₃), so the thickness and mechanical compliance of the artificial SEI can be investigated.
Katherine Jungjohann SNL-ALBQ (DOE NEES EFRC & CINT)	Investigate the Li morphology using sealed liquid cell for in situ scanning transmission electron microscopy (STEM), and investigate the effect of artificial SEI coating on morphology at nano-meter scale .
Yan Yao University of Houston	Compare Li and Mg plating morphology
Jie Xiao PNNL and U. Arkansas	Investigate the effect electrolyte additives and their role on SEI.

Proposed Future Research

- Develop an explicit SEI dendrite growth model to capture the internal structures of SEI.
- Predict the electron transport at grain boundaries
- Predict what dopants can avoid surface/grain-boundary electron trapping
- Experimentally vary the modeling prediction that a coating layer, such as LiPON, between the Li/LLZO, will be more efficient in resisting Li dendrite.
- Modeling and Experiments jointly design effective combinations (bulk solid electrolyte and surface coating) to improve the cycling efficiency and life of lithium rechargeable batteries.

Conclusions

- The internal defect surfaces (pores, grain boundaries, and junction) and their electron conducting properties are important to determine the Li dendrite growth inside of the solid electrolyte
- The surfaces have a smaller band gap than the bulk and trap excess electrons, in LLZO and Li_2O
- Solid electrolytes with finer grain size or higher volumetric percentage of internal defect surface have a higher probability of isolated Li nucleation. This causes an abrupt increase in dendrite growth depth and rate.
- The DFT predicted resistance of solid electrolytes to Li dendrite growth inside was ranked as: $\text{Li}_2\text{PO}_2\text{N} > \beta\text{-Li}_3\text{PS}_4 > \text{LATP} > \text{LLZO}$. The results are consistent with the experimental results in the literature.
- Successfully transferred the learning from solid electrolytes to SEI design in the liquid electrolyte. (dendrite resistance: $\text{Li}_2\text{S} > \text{Li}_2\text{O}$)
- Experimentally stabilized the SEI of Li metal electrode with sulfite-based additives by forming Li_2S , which is also mechanically more stable due to its volume compatibility with Li.

Acknowledgements

- Patricia Smith, Tien Duong, and Walter (Jerry) Parker for program management.
- Dr. Yunsong Li, MSU, (Li/SEI/liquid electrolyte atomistic modeling)
- Zhe Liu, PSU, (phase field development and modeling)
- Hong-Kang Tian, MSU, (solid electrolyte DFT modeling)
- Jiagang Xu, GM, (experimental work).

Publications

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2. Tian, H.K., Xu, B., Qi, Y., Computational Study of Li Nucleation Tendency in LLZO and Rational Design of Interlayer Materials to Prevent Li Dendrites, Journal of Power Source 382, 79-86 (2018)
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5. Z. Liu, P. Lu, Q. Zhang, X. Xiao, Y. Qi and L.-Q. Chen, “A Bottom-up Formation Mechanism of Solid Electrolyte Interphase (SEI) Revealed by Isotope-Assisted Time-of-Flight Secondary Ion Mass Spectrometry (TOF SIMS)”. J. Phys. Chem. Lett., 9 5508-5514 (2018).
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10. J. Xu, H.-K. Tian, J. Qi, Y. Qi, Q. Zhang, X. Xiao. “Mechanical and Electronic Stabilization of Solid Electrolyte Interphase with Sulfite Additive for Lithium Metal Batteries”, J. Electrochem. Soc. (submitted)
11. Z. Liu, Y. Li, Y. Ji, Q. Zhang, X. Xiao, Y. Yao, L.-Q. Chen, and Y. Qi, “Atomically-Informed Phase-field Modeling of Li and Mg Electrodeposition Morphologies”. (submitted)

Presentations

- 10 presentations at conferences including ACS, ECS, MRS, AICHE